



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) Publication number:

0 636 654 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 94202210.4

(51) Int. Cl. 6: C08L 53/02, C09J 153/02,

(22) Date of filing: 28.07.94

C08K 5/00, C08K 5/13,
C08K 5/37, // (C08K5/00,5:524,
5:134),(C08K5/00,5:524,5:378)

(30) Priority: 28.07.93 EP 93202235

(71) Applicant: SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)

(43) Date of publication of application:
01.02.95 Bulletin 95/05

(72) Inventor: van Westrenen, Jeroen
Badhuisweg 3
NL-1031 CM Amsterdam (NL)
Inventor: Veurink, Jacqueline Margaretha
Badhuisweg 3
NL-1031 CM Amsterdam (NL)
Inventor: van Dongen, Arie
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(54) Block copolymer composition, a process for its preparation and a hot melt adhesive comprising said composition.

(57) Block copolymer composition, comprising:

(a) 100 parts weight of a linear styrene/isoprene/styrene triblock copolymer, said copolymer having a styrene content in the range of from 10 to 50% by weight based on the total weight of block copolymer, and apparent total molecular weight in the range of from 5,000 to 300,000, said block copolymer composition having free poly(styrene) content of at most 6% and being obtainable by anionic sequential polymerization of styrene and isoprene in a solvent comprising of cyclopentane and/or cyclohexane, optionally in combination with second initiation to provide triblock copolymer being mixed with a predetermined amount of <+ 40 wt% of diblock copolymer; termination of the living block copolymer(s) with a proton donating terminating agent; and recovery of the final block copolymer(s) from the solvent solution by hot water and/or steam coagulation dewatering and/or drying and/or mixing in a predetermined well adjusted amount of similar block containing diblock copolymer, the final block copolymer composition having a solution viscosity in toluene (25 wt%) at 25 °C in the range of from 0.1 to 3

(b) 0.1 to 5 parts by weight of a stabilizer set comprising:

I one or more specific UV stabilizer, and one or more phosphite antioxidants, and adhesive hot melt compositions containing said composition.

EP 0 636 654 A1

The present invention relates to a block copolymer composition, a process for preparation thereof and an adhesive comprising said composition. More in particular, the present invention relates to a linear block copolymer composition, which can be suitably applied in hot melt adhesive compositions and which is colour stable and heat resistant during preparation of the adhesive composition and the processing thereof.

5 Styrene-conjugated diene block copolymers presently form a predominant key building block for hot melt pressure sensitive adhesive compositions.

As was known from e.g. "New Styrene Block Copolymers for Tape and Label use", F.C. Jagisch and J.M. Tancrede, PSCT Seminar Proceedings, May 1990, it has been generally accepted that a majority of styrene-conjugated diene block copolymers (further to be mentioned SBC's) to be used in hot melt pressure 10 sensitive adhesive compositions are formed by block copolymers of the structures ABA or $(AB)_nX$, wherein A represents a polystyrene block and B represents a poly(conjugated diene) and more preferably poly-(butadiene), poly(isoprene), poly(butadiene/isoprene) or ethylene/butylene random copolymer. Three dominant commercial preparation methods for such SBC's have been developed:

15 (a) the traditional coupling method, involving the steps of synthesis of relatively low molecular weight poly(styrene) polymer blocks by monofunctional anionic initiation of styrene, addition of one or more conjugated dienes to form "living" poly(styrene-conjugated diene) segments or diblocks, and coupling these anionic living diblocks to yield linear styrene-conjugated diene-styrene copolymer or - by using multifunctional coupling agents - multiarmed or radial copolymers, or

20 (b) sequential synthesis of a linear triblock copolymer ABA by initial synthesis of a diene midblock using a difunctional initiator, wherein the chain is growing from the center outward in both directions, addition of styrene which reacts with the dienyl anion chain ends to form polystyrene endblocks, and termination with a suitable proton donor, and

25 (c) sequential synthesis of a linear triblock copolymer ABA by initial synthesis of a living polystyrene block through a monofunctional initiator, addition of conjugated diene and completing its polymerization, addition of a second portion of styrene and completing its polymerization, and termination with a suitable proton donor.

It will be appreciated that an inherent consequence of preparation method (a) is the presence of a significant amount, usually ten percent or more, of uncoupled terminated diblock, since the coupling process does not provide 100 percent conversion.

30 Whereas this diblock content seemed to have little effect on quick stick or peel strength, said low molecular weight, non-cross-linked or non-load bearing diblock components have appeared to reduce the holding power (shear strength) and elevated temperature performance, as indicated by Shear Adhesion Fail Temperature (SAFT) in some degree.

35 However, the reduction of the melt viscosity caused by such diblock components, may be regarded as a desirable aspect.

On the other hand, it was known that specific measures had to be taken during the manufacture of said SBC's, intended to be used in hot melt adhesive compositions. Said SBC's had to be colour stable and heat resistant under preparation and processing conditions of the hot melt adhesive compositions, whereas said SBC's had also to retain their other physical properties.

40 In particular there was still a strong need for improved colour stable and heat resistant SBC's, the preceding polymer chains of which contain terminal alkali metal, resulting from the initiation of the polymerization.

A great variety of proposals was made to solve this problem, in general directed on the avoidance of the use of specific halogen-containing coupling agents, the use of specifically selected antioxidant additives 45 to stabilize the poly(conjugated diene) phase during the polymer transformation stage and/or the use of specifically selected acids to be used for the neutralization of the living terminal alkali metals and in particular lithium resulting from the initiation.

For example, from the European patent No. 0309434 was known a process for decolorizing styrene-conjugated diene block copolymers, having a relatively high styrene content to yield perfectly transparent 50 copolymers, having good impact strength properties and satisfying the demanding criteria set by the food-supply industry, comprising the treatment of polymer derived from living chains which end with an alkali metal, with a specific group of sulphur containing carboxylic acids and more preferably thiadipropionic acid or thiodiglycolic acid or methylene bis(thiopropionic acid) or methylene bis(thioacetic acid).

The starting copolymers to be treated with these carboxylic acids were predominantly obtained by 55 coupling of living block polymers by a large variety of listed coupling agents.

As antioxidants were used 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT); tris(p-nonylphenyl)-phosphite (TNPP) and octadecyl ester of 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene propanoic acid (IR-GANOX 1076) (IRGANOX is a trade mark).

From European patent application No. 0379951 a process was known for the preparation of SBC's by anionic polymerization using an alkali metal-containing initiator, whereby the polymerization is terminated by adding an aliphatic or aromatic compound containing one or two hydroxyl groups after which the polymer cement is neutralized by adding an organic acid halide. Finally, the polymer is recovered. In the comparative examples of said European patent application, neutralization is achieved by adding oleic acid or glacial acetic acid in toluene solvent, while an antioxidant package consisting of TNPP and the triazine derivative 4-((4,6-bis(octylthio)-s-triazin-2-yl)amine)-2,6-di-t-butylphenol was also included in said block copolymer composition. However, the comparative organic acids were shown to be inferior as compared to the proposed organic acid halides and this teaching could lead a person skilled in the art only away from the application of organic acids as such as neutralizing agents.

From European patent application No. 0479754 a process was known for decolorizing SBC's, obtained through an initiation step of the copolymerization with alkali metal catalysts, comprising the treatment of the copolymer with a monocarboxylic acid of the formula R-COOH, wherein R represents a linear or branched aliphatic, cycloaliphatic or alkenic hydrocarbon group containing from 2 to 4 carbon atoms, said treatment being performed after the actual termination of the anionic polymerization with a separate active hydrogen containing reagent.

In addition to said acids, small amounts of anti-oxidants such as TNPP and IRGANOX 1076 were added to the block copolymer, having a weight ratio between styrene and butadiene of > 1 and in particular 75/25.

From Japanese patent application (Kokai) No. 63-179953 a process was known for the preparation of a polymer composition, comprising the steps of addition of 0.05 to 5 equivalents of one or more organic acids, based on the organolithium compound initially used as initiator for the polymerization in organic solvent solution of conjugated diene and/or vinyl aromatic hydrocarbon, in which polymer solution may also be present a terminator, and then incorporation of 0.05 to 5 parts by weight based on 100 parts by weight of said polymer of at least one phenol compound selected from the group formed according to three specified formulae covering a number of commercially available anti-oxidants of the trade name SUMILIZER (SUMILIZER is a trade mark).

From US patent No. 4,403,074 a process was known for the preparation of a resinous copolymer of at least one conjugated diene and at least one hydrocarbon monovinyllarene, which comprises copolymerizing at least one hydrocarbon conjugated diene and at least one monovinyllarene, employing a hydrocarbon solvent, alkali metal initiator, and solution polymerization conditions, thereby producing an alkali metal terminated copolymer, coupling with a multifunctional coupling agent to produce a coupled polymer in said solvent, wherein the improvement comprises treating the coupled polymer in said solvent, with an effective amount of at least one linear alkane dicarboxylic acid selected from the group consisting of saturated aliphatic diacids having from 2 to 16 carbon atoms and in particular selected from oxalic acid, malonic acid, glutaric acid, adipic acid, suberic acid, sebacic acid, undecanedioic acid, dodecanedioic acid and mixtures thereof.

In addition to such dicarboxylic acids, usually applied in amounts of from 0.02 to 2 parts per 100 parts of copolymer, also small amounts of TNPP and of 2,6-di-tert.butyl-p-cresol were added.

From the Japanese patent application J 60-231717 was known to prepare transparent, devitrification resistant polymers from a solution obtained by polymerizing conjugated diene and/or vinyl aromatic compound using organolithium compound in a hydrocarbon solvent. Said polymer preparation comprised:

- (a) adding a stabilizer, selected from a phenol derivative, organic phosphate, amine or sulphur anti-oxidant in amounts of from 0.001-10 parts by weight per 100 parts by weight of polymer, and a terminator selected from water, methanol, ethanol, ethylene glycol, propylene glycol and glycerine to a polymer solution,
- (b) removal of the solvent from the solution and then,
- (c) mixing a higher fatty acid of 10 carbon atoms or more and/or rhodinic acid and a hydroxycarboxylic acid.

The fatty acid and/or rhodinic acid was used as 0.01-0.5 (preferably 0.05-0.3) parts by weight per 100 parts by weight of the polymer, while the hydroxycarboxylic acid was used in amounts of 0.01-0.2 parts by weight per 100 parts by weight of the polymer. Preferred higher fatty acids were mentioned to be capric acid, lauric acid, stearic acid or behenic acid, while the hydroxycarboxylic acid was selected from glycolic acid, tartaric acid or citric acid.

It will be appreciated that the application of the described combination of acids will give rise to additional costs, as the additional acids are rather expensive and the processing will be more complicated and less reproducible.

From US patent No. 4,835,200 a hot melt adhesive composition was known, possessing colour stability and resistance to heat degradation, oxidation and skin formation, containing a block copolymer comprising

at least two monoalkenyl arene polymer end blocks A and at least one elastomeric conjugated diene polymer midblock B and more in particular two polystyrene blocks and at least one poly(butadiene) or poly(isoprene) block prepared using a bromide based coupling agent, a tackifying resin and an effective amount of a stabilizer composition.

- 5 The stabilizer composition contains a thio-compound, a phenolic antioxidant, a tris-(nonylated phenyl)-phosphite, and an aliphatic compatible epoxy compound, which composition was indicated to be a synergistic stabilizer.

As thio-compounds were used Irganox 565;

as examples of phenolic antioxidants were used Ionol, Irganox 1010 and Irganox 1330;

- 10 as examples of phosphite stabilizer were used Ultranol 626, Irgaphos 168 and Polygard HR, the latter of which being preferred; and

as examples of epoxy stabilizer were used Drapex, Araldite GY 6010 and Epon 2004, of which Drapex being preferred (Ionol, Irganox, Polygard, Irgaphos, Drapex, Araldite and Epon are trade marks).

- 15 From e.g. US patent No. 5,145,896, more recently became known a method for reducing the colour of a hot melt adhesive formulation, comprising a block polymer of a conjugated diene and a vinyl aromatic compound which contains residual LiBr, LiCl or LiJ salts, which comprises adding to the formulation an amount of an alkyltin compound, selected from the group consisting of mercaptides, mercaptocarboxylates and carboxylates sufficient to reduce colour formation.

- 20 From US patent No. 5,171,791 was known an adhesive formulation, comprising a polymer prepared by means of a process, comprising anionic sequential polymerization of monomers selected from the group consisting of monovinylidene aromatic monomers and alkadienes with an organolithium containing anionic initiator;

- 25 terminating the polymerization by contacting the resulting reaction mixture with a proton donating terminating agent selected from the group consisting of water and alcohols, resulting in the formation of a lithium salt of the terminating agent; and

neutralizing the alkali metal salt by contacting the reaction mixture obtained with from 0.01 to 10.00 equivalents phosphoric acid per equivalent of initiator.

- 30 As stabilizers were used in the working examples 0.3 weight percent of Irganox 1010 and 0.3 weight percent of trisnonylphenylphosphite stabilizer;

0.5 weight percent of Irganox 565 and 0.5 weight percent of Irgaphos 168 [tris(2,4-di-tert.butylphenyl)-phosphite]; and 0.5 weight percent of Irganox 565 and 0.5 weight percent of Irgaphos 168 respectively.

- 35 In spite of the great variety of proposals directed to the preparation of colour stable and heat resistant SBC's, there has still remained a growing need for providing said SBC compositions, which show an attractive combination of colour stability, shear stability, heat stability and adhesive properties when applied in hot melt adhesive compositions, in an economically attractive way.

- Therefore it is an object of the present invention to provide such a block copolymer composition aimed at and as specified hereinbefore.

- Moreover, it is also an object of the present invention to provide a process for the preparation of said block copolymer compositions aimed at.

- 40 Another object of the present invention is formed by hot melt adhesive compositions, containing said block copolymer compositions.

- It will be appreciated from the hereinbefore discussed publications that a clear teaching which was generally accepted up to now by persons skilled in the art, was to apply acids after the termination (including coupling) of the living block copolymer and/or before the addition of the selected set of 45 stabilizers, to obtain block copolymer compositions showing allegedly acceptable properties when used in hot melt adhesive compositions.

- As a result of extensive research and experimentation there have been surprisingly found block compositions, showing the hereinbefore specified combination of properties.

- Accordingly, the present invention relates to a block copolymer composition, comprising;
- 50 (a) 100 parts by weight of a linear triblock copolymer, comprising two terminal predominantly poly(styrene) blocks having an apparent molecular weight in the range of from 5,000 to 25,000 and one predominantly poly(isoprene) midblock, as sole or major component, said triblock copolymer having a styrene content in the range of from 10 to 50% by weight based on the total weight of block copolymer, an apparent total molecular weight in the range of from 5,000 to 300,000 and preferably from 100,000 to 55 270,000, said block copolymer composition having a free poly(styrene) content of at most 6% and preferably < 2.5%, and being obtainable by anionic sequential polymerization of predominantly styrene and isoprene, in a solvent comprising cyclopentane or cyclohexane as main solvent, said anionic sequential polymerization optionally being combined with reinitiation or mixing in a predetermined well

adjusted amount of diblock copolymers containing similar blocks, to provide a predetermined and well adjusted minor amount of diblock copolymer, containing similar blocks, (< 40 wt.% relative to the weight of the total weight of block copolymers); termination of the living block copolymer(s) with a proton donating terminating agent, such as alcohol or a mono-epoxy compound, such as ethylene oxide, propylene oxide, or phenylglycidyl ether; and recovery of the final block copolymer(s) from the solvent solution by hot water and/or steam coagulation in the absence of oxygen, at a temperature in the range of from 85 to 120 °C and preferably in the range of from 90 to 110 °C, followed by dewatering and/or drying and/or mixing a predetermined well adjusted amount of similar blocks containing diblock copolymer, the final block copolymer composition having a solution viscosity in toluene (25 wt%) at 25 °C in the range of from 0.1 to 3 and preferably from 0.5 to 2.

(b) 0.1 to 5 parts by weight and preferably from 0.2 to 1 parts by weight of a stabilizer set comprising:
a specific UV stabilizer, selected from the group consisting of octadecyl ester of 3,5 bis(1,1-dimethylethyl)-4-hydroxy benzene propanoic acid (IRGANOX 1076), 2,4-bis(n-octylthio)6-(4-hydroxy-3,5-di-tert-butyl anilino)-1,3,5 triazine (IRGANOX 565), 2-tert-butyl-6(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (SUMILIZER GM) and combinations thereof, and a phosphite antioxidant, selected from tris(nonylphenyl)phosphite (TNPP), tris(mixed mono- and di-nonylphenyl)phosphite (POLYGARD HR), bis(2,4-di-tert.butyl phenyl)pentaerithritol diphosphite, (ULTRANOX 626), tris(2,4-ditert.butylphenyl)-phosphite (IRGAFOS 168) and combinations thereof. (IRGANOX, POLYGARD, ULTRANOX, SUMILIZER and IRGAFOS are trademarks).

A preferred phosphite antioxidant is tris(mixed mono- and di-nonylphenyl phosphite (POLYGARD HR).

The styrene content of the linear block copolymer can not be too high, i.e. higher than 50% by weight, as in such a case the block copolymer would be too resinous and hard to be suitably applied in hot melt adhesives. On the other hand, a too low content of styrene compound, i.e. lower than 10% by weight, is also undesired because then the block copolymer will be too soft to handle. It is preferred that the vinyl aromatic compound is present in the block copolymer in an amount in the range of from 13 to 35% by weight.

In particular the poly(isoprene) blocks of the triblock copolymer compositions according to the present invention have average apparent molecular weights in the range of from 80,000 to 250,000, and preferably in the range of from 100,000 to 200,000, whereas the poly(styrene) blocks have average apparent molecular weights ranging from 5,000 to 25,000 and preferably from 9,000 to 15,000.

With the term "predominantly poly(styrene)" and "predominantly poly(isoprene)" as used throughout the specification, is meant that substantially pure homopolymer blocks, copolymer blocks derived from styrene and structurally related comonomers (e.g. a mixture of a major part of styrene and a minor part (< 20 wt.% of α-methylstyrene, o-methylstyrene, p-methylstyrene, p-tert.butyl styrene; 1,3-dimethylstyrene or mixtures thereof), or from isoprene and structurally related comonomers (e.g. a mixture of a major part of isoprene and a minor part of butadiene; 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene or 1,3 hexadiene), or copolymer blocks of structurally not related comonomers, such as styrene in a major amount and isoprene in a minor amount (< 15 wt.%), can be produced as constituting elements of the total block copolymers.

The predominantly poly(isoprene) blocks can be derived from as well substantially pure isoprene

feedstock as lower concentrate isoprene feedstocks (> 50 wt% isoprene) containing inert C₅ paraffins and mono-olefins. The term inert means that in the isoprene containing mixture, polymerization killers have been inactivated e.g. by sodium treatment.

With the term "diblock copolymers containing similar blocks" as used throughout the specification, is meant diblock copolymers, the blocks of which are constituted by the same monomer(s) as defined for the triblock copolymers and the total apparent molecular weights of which are in the range from 50,000 to 170,000 and preferably from 70,000 to 150,000.

However preferably block copolymers containing substantially pure poly(styrene) and substantially pure poly(isoprene) are prepared and used.

More preferably the apparent molecular weight of the complete triblock copolymers are in the range of from 150,000 to 250,000.

With the term "apparent molecular weight" as used throughout this specification, the molecular weight of a polymer is meant, except polystyrene itself, as measured with gel permeation chromatography (GPC) using polystyrene calibration standards as described in ASTM D 3536.

It will be appreciated that the finally used block copolymers are consisting of substantially pure triblock copolymers or of mixtures of said triblock copolymers and a predetermined well adjusted amount of corresponding diblock copolymers. Such mixtures of block copolymers are obtainable by a polymerization process as specified in the copending European patent application No. 93200909.5, filed 30.3.93, or by mixing in such a predetermined well adjusted amount of corresponding diblock copolymers into the triblock

copolymer before or after termination and/or recovery.

The last mentioned European application discloses a process for the preparation of a block copolymer composition, said process comprises the subsequent steps of:

- (1) polymerizing vinyl aromatic monomer and in particular styrene in an inert hydrocarbon solvent in the presence of an organolithium initiator until substantially complete conversion;
- (2) adding conjugated diene monomer, and in particular isoprene, to the polymerization mixture and allowing said conjugated diene monomer to polymerize until substantially complete conversion;
- (3) adding a second portion of organolithium initiator, followed by the addition of a second portion of conjugated diene monomer and allowing said conjugated diene monomer to polymerize until substantially complete conversion;
- (4) adding a second portion of vinyl aromatic monomer and allowing said monomer to polymerize until substantially complete conversion; and
- (5) adding a terminating agent.

As terminating agent can be used primary alcohols or secondary alcohols, e.g. methanol, ethanol, 2-

ethyl hexanol, or a monoepoxy compound, e.g. ethylene oxide, propylene oxide or phenylglycidyl ether. Alcohols are the more preferred terminating agents.

The weight ratio between the UV stabilizer on the one hand and the phosphorus containing anti-oxidant on the other hand should be within the range of from 1 to 0.05 in order to achieve the more attractive block copolymer compositions. The best results are achieved when said weight ratio is in the range of from 0.5 to 0.1.

It will be appreciated that another aspect of the present invention is formed by hot melt adhesive compositions containing said block copolymer compositions.

Accordingly, the present invention also relates to a hot melt adhesive composition comprising:

- (a) 100 parts by weight of the block copolymer composition as described hereinbefore;
- (b) 20-400 parts by weight of a tackifying resin; and
- (c) 0-200 parts by weight of a softening agent.

The primary tackifying resins useful in the practice of this invention include hydrocarbon resins, synthetic polyterpenes, rosin esters and natural terpenes which are semi-solid or solid at ambient temperatures, and soften or become liquid at temperatures ranging generally from about 70 °C to about

135 °C, preferably from about 85 °C to about 120 °C. Exemplary of the primary tackifying resins are compatible resins such as (1) natural and modified rosins such as, for example, gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, and polymerized rosin; (2) glycerol and pentaerythritol esters of natural and modified rosins such as, for example, the glycerol ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-modified pentaerythritol ester of rosin; (3) copolymers and terpolymers of natural terpenes, e.g., styrene/terpene and alpha methyl styrene/terpene; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from about 80 ° to 150 °C; the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons, such as the bicyclic monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low

temperatures; also included are the hydrogenated polyterpene resins; (5) phenolic modified terpene resins and hydrogenated derivatives thereof such as, for example, the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70 ° to 135 °C; the latter resins resulting from the polymerization of monomers consisting primarily of olefins and diolefins; also included are the hydrogenated aliphatic petroleum hydrocarbon resins; (7) aromatic petroleum hydrocarbon resins, and mixed aromatic and aliphatic paraffin hydrocarbon resins, and the hydrogenated derivatives thereof; (8) aromatic modified alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof; and (9) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof. The preferred primary tackifying resins for use in the practice of this invention are represented by sub-paragraphs (1), (3) and (7), supra.

Suitable secondary tackifying resins are those named species wherein the resin is a liquid at ambient temperature.

Various softening agents are useful in the practice of this invention. The softening agent can be used in place of or in combination with the secondary tackifier to reduce viscosity and improve tack properties. Softening agents which have been found useful include olefin oligomers and low molecular weight polymers as well as vegetable and animal oil and their derivatives. The petroleum derived oils which may be employed are relatively high boiling materials containing only a minor proportion of aromatic hydrocarbons (preferably less than 30% and, more particularly, less than 15% by weight of the oil). Alternately, the oil may be totally non-aromatic. The oligomers may be polypropylenes, polybutenes, hydrogenated

polyisoprene, hydrogenated polybutadiene, polypiperylene and copolymers of piperylene and isoprene, or the like having average molecular weights between about 350 and about 10,000. Vegetable and animal oils include glyceryl esters of the usual fatty acids and polymerization products thereof.

According to a preferred embodiment of the block copolymer compositions of the present invention, the 5 block copolymer constituents are prepared by sequential polymerization, optionally in combination with reinitiation, using a monolithium alkyl compound as initiator and optionally as second initiator, and more preferably sec-butyllithium or n-butyllithium, in a solvent comprising cyclopentane or cyclohexane, termination of the living polymer(s) with water, alcohol, hydrogen, mono epoxy compounds and preferably alcohols and more preferably methanol, followed by recovery of the block copolymer(s) by hot water and/or steam 10 coagulation and dewatering and/or drying.

The set of stabilizing compounds can be added after termination of living polymers or at any later stage of the manufacturing process, but preferably just after termination.

The solvent to be used for the preparation of the block copolymer(s), are preferably substantially pure cyclohexane or substantially pure cyclopentane, or mixtures of one of these solvents as main solvent with a 15 minor amount (< 50 wt%) of linear or branched alkanes having 5 to 7 carbon atoms such as n-hexane, isopentane or n-pentane.

Particularly suitable are cyclohexane, cyclohexane/n-hexane mixtures, cyclohexane/isopentane/n-hexane mixtures, cyclopentane and cyclopentane/isopentane mixtures.

Cyclohexane/isopentane mixtures, substantially pure cyclohexane or cyclopentane are preferred and 20 cyclopentane is the most preferred.

It will be appreciated that the preparation of the triblock constituent, optionally mixed with a corresponding diblock copolymer, obtainable by reinitiation, can be carried out in one single reactor equipped with a recycling condenser or in a dual reactor system.

The drying of the block copolymer to remove the last amounts of adhering water can be carried out in a 25 fluid bed dryer, a hot belt dryer or in a closed evaporator/dryer, wherein a rotating shaft provided with several heated self-cleaning arms, which move along fixed partition plates.

It will be appreciated that advantages related to the block copolymer compositions of the present invention are formed by the avoidance of expensive and sometimes corrosive acids, which in addition may cause contamination of the block copolymers with heavy metals.

30 The invention is further illustrated by the following examples without restricting the scope of the invention to these specific embodiments.

In these examples the molecular weight of the block copolymers prepared is determined by Gel Permeation Chromatography (GPC) using polystyrene calibration standards as described in ASTM D 3536. The polystyrene content of the block copolymers is determined according to the method described in 35 ASTM D 3314.

From the data obtained by these methods other data such as the molar weight ratio of the respective polyisoprene blocks in the triblock and diblock copolymers and the styrene weight ratio triblock/diblock are derived.

40 Example 1

A batch of about 4000 kg of a pure triblock copolymer poly(styrene-isoprene-styrene), with equal styrenic endblocks containing 81 wt.% of polyisoprene centre block and 19 wt.% polystyrene in the form of terminal blocks and having a total apparent mol. weight of 206,500, was prepared in cyclopentane solution 45 in a single stainless steel reactor by means of sequential polymerization at a temperature varying between 55-60 °C, using sec.butyllithium (27.5 mol) as anionic initiator. The applied technical cyclopentane had a purity of at least 97% and had previously been distilled and treated with alumina. Isoprene monomer was added to the polymerization carried out under evaporative cooling. Before the polymerization was started, the styrene-solvent mixture was scavenged by addition of initiator.

50 Thereafter the catalytic amount of initiator was added and after substantially complete conversion, isoprene was added and subsequently by styrene. The living block copolymer was terminated with methanol (10%, molar excess to BuLi) and a set of antioxidants/stabilizers was added thereafter, comprising trisnonylphenylphosphite (POLYGARD HR) and 2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-tert.butylanilino)-1,3,5-triazine (IRGANOX 565) in amounts of 0.4 wt.% and 0.09 wt.% respectively relative to the weight of 55 the block copolymer.

The polymer was recovered by steam and/or hot water coagulation at a temperature not exceeding 95 °C. The wet polymer mass was dewatered by using a WELDING ENGINEER equipment, applying a head temperature not exceeding 90 °C.

The polymer was dried in an ARTOS hot air dryer comprising three compartments wherein the respective band speeds were in the range of from 10 m/sec to 1.2 m/sec and the respective temperatures 70 °C, 70 °C and 35 °C.

The relevant properties of the obtained pure triblock copolymer have been listed in the following table.

5

Example 2

A batch of about 4000 kg of a triblock copolymer poly(styrene-isoprene-styrene) copolymer having $M_{app} = 153,000$, and bound styrene content of 19% composed by 8.5%, and 10.5% in the respective poly(styrene)blocks, mixed with a predetermined required amount of 27 wt.% or diblock copolymer ($M_{app} = 140,000$) was prepared under similar conditions as specified in example 1, except that the full sequential polymerization was combined with a second initiation at the start of the isoprene polymerization by dosing a second portion of sec.butyllithium initiator to start novel polymer chains, which react simultaneously with the chains already formed.

10 The first amount of sec. butyllithium was 21.3 mol and the second amount of sec. butyl lithium was 12.5 mol. The properties of the obtained triblock-diblock copolymer mixture have been listed in the following table.

Example 3

20

A batch of about 4000 kg of a similar triblock poly(styrene-isoprene-styrene) copolymer having $M_{app} = 220,000$ and a bound styrene content of 23%, mixed with a predetermined required amount of 26% diblock copolymer ($M_{app} = 107,000$) was prepared under similar conditions as specified in example 1, using 17.5 mol of sec butyllithium, except that the full sequential polymerization was combined with a second initiation during the isoprene polymerization by dosing a second portion of sec.butyllithium initiator (12.3 mol).

25 The properties of the obtained triblock-diblock copolymer mixture have been listed in the following table.

Example 4

30

A batch of about 2500 kg of a triblock-diblock copolymer mixture of styrene and isoprene was prepared having a bound styrene content of 14% and a diblock copolymer content of 17%, the apparent total molecular weights of triblock and diblock copolymers being 216,000 and 110,000 respectively. The polymerization is performed, in a two reactor system, using as solvent a 50:50 mixture cyclohexane/isopentane, by means of a full sequential polymerization in combination with a reinitiation second amount of sec. butyllithium 5.4 mol during the polymerization of isoprene block.

35 The living polymer was terminated with 2-ethylhexanol. A set of stabilizers, comprising POLYGARD HR and IRGANOX 565 was added in an amount of 0.4 wt% and 0.1 wt% respectively.

The polymer was recovered by steam and/or hot water coagulation the temperature during which was not exceeding 115 °C.

40 The wet polymer mass was dewatered by using a Welding Engineer Equipment applying a head temperature not exceeding 90 °C.

The polymer was dried in an ARTOS hot airdryer under conditions as specified in example 1.

Examples 5-8

45 A batch of about 4000 kg of triblock copolymers (styrene-isoprene-styrene) as obtained according to the examples 1-3 was prepared with the exception that as stabilizer combination was used:

50

IRGAFOS 168 ULTRANOX 628 TNPP HR IRGAFOS 168	IRGANOX 565, IRGANOX 565, SUMILIZER GM, SUMILIZER GM.
---	--

55

The properties of the obtained triblock-diblock copolymer mixtures have been listed in the following table.

Table

Examples	Sol. visc. (Pa.s) A	Breakdown (%) B	Colour C
1	1.1	51	white
2	0.6	87	white
3	1.1	55	white
4	1.9	58	white
5	1.1	54	white
6	1.1	55	white
7	1.1	53	white
8	1.1	51	white
Comparative Examples	Sol. visc. (Pa.s) A	Breakdown (%) B	Colour C
1. V4111°	1.0	71	white
2. V4113°	1.5	48	white
3. Sol. T 193 B*	0.6	62	slight yellow

20 °: These block copolymers are commercially available from DEXCO.

*: This block copolymer is commercially available from Enichem.

A: Solution viscosity is measured in toluene at 25 °C in a 25 wt% toluene solution.

B: The breakdown of the polymer is determined by the ratio between the square root of the solution viscosity of the polymer after and before the testing in a Brabender mixer, i.e. $100 \cdot \sqrt{(\text{sol. visc. after/sol. visc. before})}$.

Brabender test procedure: the polymer material is added pure in a cup. Temperature of the cup is 140

• C. The cup is filled with polymer for 4/5, leaving 1/5 of open space containing air. The blades of the mixer is set at 50 rpm. Due to shear, the temperature of the polymer mass of the sample increases to 160 °C. The test run is performed for 30 minutes. Due to the constant speed of the blades higher viscosity polymers receive more shear and are prone to degrade more than low viscosity ones. Therefore, only polymers with comparable viscosity can be compared with each other e.g. example 4 with comparative example 2 and 3.

35 C: Visual determination of the colour.

Claims

1. Block copolymer composition, comprising:

40 (a) 100 parts weight of a linear triblock copolymer, comprising two terminal predominantly poly(styrene) blocks having an apparent molecular weight in the range of from 5,000 to 25,000 and one predominantly poly(isoprene) midblock, as sole or major component, said triblock copolymer having a styrene content in the range of from 10 to 50% by weight based on the total weight of block copolymer, and apparent total molecular weight in the range of from 5,000 to 300,000, said block copolymer composition having free poly(styrene) content of at most 6% and being obtainable by anionic sequential polymerization of predominantly styrene and isoprene, in a solvent comprising of cyclopentane and/or cyclohexane as main solvent, said anionic sequential polymerization optionally being combined with reinitiation or mixing in a predetermined well adjusted amount of diblock copolymer containing similar blocks, to provide a predetermined and well adjusted minor amount of diblock copolymer, containing similar blocks, (< 40 wt%) relative to the weight of the total weight of block copolymers; termination of the living block copolymer(s) with a proton donating terminating agent such as alcohol or a mono-epoxy compound such as ethylene oxide or propylene oxide or a phenylglycidyl ether; and recovery of the final block copolymer(s) from the solvent solution by hot water and/or steam coagulation in the absence of oxygen, at a temperature in the range of from 85 to 120 °C, followed by dewatering and/or drying and/or mixing in a predetermined well adjusted amount of similar block containing diblock copolymer, the final block copolymer composition having a solution viscosity in toluene (25 wt%) at 25 °C in the range of from 0.1 to 3 and preferably from 0.5 to 2

(b) 0.1 to 5 parts by weight of a stabilizer set comprising:

I a specific UV stabilizer, selected from the group consisting of octadecyl ester of 3,5 bis (1,1 dimethylethyl)-4-hydroxy benzene propanoic acid (IRGANOX 1076), 2,4-bis(n-octylthio)6-(4-hydroxy-3,5-di-tert-butyl anilino)-1,3,5 triazine (IRGANOX 565) and 2-tert.butyl-6-(tert.butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (SUMILIZER GM and combinations thereof; and II phosphite antioxidant, selected from tris-(nonylatedphenyl)phosphite (TNPP), tris(mixed mono- and di-nonylphenyl)phosphite such as POLYGARD HR, bis(2,4-di-tert.butyl phenyl)pentaerithritol diphosphite (ULTRANOX 626) or tris(2,4-ditert.butylphenyl)phosphite (IRGAFOS 168) and combinations thereof.

- 5 2. Block copolymer composition according to claim 1, characterized in that it contains tris(mixed mono- and di-nonylphenyl)phosphite as phosphite anti-oxidant.
- 10 3. Block copolymer composition according to claims 1 and 2, characterized in that it contains from 0.2 to 1 part by weight of a stabilizer set.
- 15 4. Block copolymer composition according to claims 1-3, characterized in that the free poly(styrene) content is less than 2.5 wt%.
- 20 5. Block copolymer composition according to claims 1-4, characterized in that the apparent total molecular weight of the triblock copolymer is in the range of from 100,000 to 270,000.
- 25 6. Block copolymer composition according to claims 1-5, characterized in that the poly(isoprene) blocks of the triblock copolymer have apparent molecular weights in the range of from 80,000 to 250,000, whereas the poly(styrene) blocks have average apparent molecular weights ranging from 5,000 to 25,000.
- 30 7. Block copolymer composition according to claim 6, characterized in that the poly(isoprene) blocks have apparent molecular weights in the range of from 100,000 to 180,000, whereas the poly(styrene) blocks have average apparent molecular weights ranging from 9,000 to 15,000.
- 35 8. Block copolymer composition, according to claims 1-7, characterized in that it contains diblock copolymers containing similar blocks, of a total apparent molecular weight in the range of from 50,000 to 170,000 and preferably from 70,000 to 150,000.
- 9. Block copolymer composition according to claims 1-8, characterized in that the block copolymer(s) contain substantially pure poly(styrene) blocks and substantially pure poly(isoprene) blocks.
- 40 10. Block copolymer composition according to claims 1-9, characterized in that triblock copolymer and diblock copolymer mixtures are obtained by means of sequential polymerization in combination of a second initiation, by addition of an additional amount of initiator during the isoprene polymerization step.
- 45 11. Block copolymer composition according to claims 1-10, characterized in that the weight ratio between the UV stabilizer and the phosphorus containing anti-oxidant is in the range of from 1 to 0.05 and preferably from 0.5 to 0.1.
- 50 12. Block copolymer composition according to claims 1-11, characterized in that the block copolymers have been produced using substantially pure cyclopentane or cyclohexane, in a single reactor equipped with a recycling condenser.
- 55 13. Hot melt adhesive compositions, comprising:
 - (a) 100 parts by weight of the block copolymer composition according to claims 1-12;
 - (b) 20-400 parts by weight of a tackifying resin, and
 - (c) 0-200 parts by weight of a softening agent.
- 14. Process for the preparation of block copolymer compositions according to claims 1-13, comprising sequential polymerization of predominantly styrene and predominantly isoprene respectively, using a

monolithium alkyl compound as initiator and optionally as second initiator and more preferably sec-butyllithium or n-butyllithium in a solvent comprising cyclopentane or cyclohexane, termination of the living polymer(s) with alcohol, water, hydrogen or mono epoxy compounds and preferably alcohols and more preferably methanol, followed by recovery of the block copolymer(s) by hot water and/or steam coagulation and dewatering and/or drying, and adding the set of stabilizing compounds.

- 5 15. Process according to claim 14, characterized in that the set of stabilizing compounds is added just after termination.
- 10 16. Process according to claims 14 and 15, characterized in that polymerization solvent is consisting of cyclohexane/isopentane mixtures or substantially, pure cyclopentane or substantially pure cyclohexane.
- 17. Process according to claims 14-16, characterized in that pure cyclopentane is used as polymerization solvent.

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 2210

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
P,Y	PATENT ABSTRACTS OF JAPAN vol. 17, no. 663 (C-1138) 8 December 1993 & JP-A-52 014 206 (DENKI KAGAKU K.K.K.) 24 August 1993 * abstract * ---	1-17	C08L53/02 C09J153/02 C08K5/00 C08K5/13 C08K5/37 //(C08K5/00, 5:524, 5:134), (C08K5/00, 5:524, 5:378)
Y	US-A-5 149 741 (ALPER ET AL.) * column 8, line 36 - line 43 * * column 9, line 1 - line 2 * * column 9, line 6 - line 7; claims; examples * ---	1-17	
Y,D	US-A-4 835 200 (ST. CLAIR) * claims 1,2,4; examples 15-16,23-24 *	1-17	
A	EP-A-0 387 671 (DOW CHEMICAL CO.) * claims 4-6,10; examples 1-7 *	1-17	
D	& US-A-5 171 791 (DOW CHEMICAL CO.) -----		
TECHNICAL FIELDS SEARCHED (Int.Cl.)			
C08L C09J C08K			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	6 October 1994	Loiselet-Taisne, S	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
A : technological background	D : document cited in the application		
O : non-written disclosure	L : document cited for other reasons		
P : intermediate document	& : member of the same patent family, corresponding document		